



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: D21C 9/10, D21H 21/32	A1	(11) International Publication Number: WO 96/20308 (43) International Publication Date: 4 July 1996 (04.07.96)
--	----	--

(21) International Application Number: PCT/US95/14995

(22) International Filing Date 16 November 1995 (16.11.95)

(30) Priority Data:
365,253 28 December 1994 (28.12.94) US(71) Applicant: MINERALS TECHNOLOGIES INC. (US/US); 405
Lexington Avenue, New York, NY 10174-1901 (US).(72) Inventor: DRUMMOND, Donald Kendall; 11 Lauren Lane,
Glenmoore, PA 19343 (US)(74) Agents: RICHARDS, John, Ladas & Parry, 26 West 61st Street,
New York, NY 10023 (US) et al(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA,
CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP,
KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD,
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD,
SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European
patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE,
LS, MW, SD, SZ, UG).**Published***With international search report.**Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.*

(54) Title: BLEACHING OF FILLED PAPER

(57) Abstract

The present invention discloses the use of bleaching agents to increase the brightness of filled paper. In the process of the present invention, filled paper is treated with bleaching agents during the papermaking process. The process may be used on all grades of paper that contain filler. However, the present invention is particularly useful on low brightness grade papers that are produced from mechanical pulps and contain a calcium carbonate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

BLEACHING OF FILLED PAPER

Field of the Invention

The present invention relates to a method for improving the optical properties of filled paper. More particularly, the present invention relates to a method for improving the brightness of paper containing calcium carbonate by treating the filled paper with bleaching agents.

Papers produced according to the process of the above invention allow papermakers to charge a premium price for the product, while obtaining improved optical properties without significantly increasing the cost of production.

The invention may be used on all grades of paper that contain filler. However, the invention is particularly useful on paper that is produced from mechanical pulps.

Background of the Invention

One of the most important characteristics of paper is the degree of whiteness of the paper. Generally, the whiter the paper, the higher the selling price. Efforts on the part of papermakers to obtain whiter papers have been directed to treatment of the pulp by subjecting it to bleaching agents such as alkaline hypochlorite. However, in

- 2 -

bleaching the pulp, large quantities of bleaching agents are required. This contributes to increased production cost, as well as inefficient use and consumption of bleaching agents.

Papermakers who produce paper from mechanical pulps lose brightness due to alkaline darkening of the pulp when fillers such as calcium carbonate are used in the papermaking process. This darkening effect restricts the use of certain fillers, such as calcium carbonate, as well as reduces the price that can be charged for papers whose optical properties are less than desired. Because of the increased cost of using current bleaching techniques, a more economical bleaching technique is required. Additionally, because of the darkening that occurs in paper that contain mechanical pulps and fillers such as calcium carbonate, a technique to regain the brightness losses in this type of paper is required.

What has been found to be novel and unanticipated by the prior art is a process for bleaching papers containing mechanical pulps and fillers such as calcium carbonate, clay, and talc.

It is therefore an object of the present invention to provide a process for brightening filled paper. Another object of the present invention is to provide an economical process for the production of quality paper produced from mechanical pulps and calcium carbonate. Yet another object of the present invention is to provide a finished paper product that is particularly useful in applications where a high degree of whiteness is required. A further object of the invention is to allow the

- 3 -

papermaker to increase the brightness of paper without the use of an expensive bleaching plant. A final object of the invention is to allow the papermaker to use calcium carbonate fillers and mechanical pulps for producing paper without suffering the effects of alkaline darkening.

These and other objects of the present invention will become apparent as further provided in the detailed specification which follows.

Prior Related Art

U.S. Pat. No. 2,150,926 discloses a process for bleaching sheet materials formed of fibrous pulp of vegetable origin by using hydrogen peroxide or substances generating hydrogen peroxide in solution.

U.S. Pat. No. 2,510,595 discloses bleaching of groundwood paper with an alkaline solution containing a per-compound, such as hydrogen peroxide, and a phosphate.

U.S. Pat. No. 2,613,579 discloses simultaneous bleaching and sizing of paper sheets with an alkaline aqueous solution of hydrogen peroxide and a wax dispersion.

According to Tang, "Stabilization of Paper Through Sodium Borohydride Treatment", American Chemical Society, Pages 212, 427-441 (1986), reducing agents, such as sodium borohydride have been used to brighten paper.

None of the above referenced subject matter in whole or in part suggests that filled paper produced with mechanical pulps can be brightened through the use of various bleaching agents.

Summary of the Invention

What has been found to be novel and unanticipated by prior art is a method for

improving the optical properties of filled paper by bleaching the paper.

The process of the present invention is useful on grades of paper that contain filler. The invention is especially useful on grades of paper that are produced from mechanical pulps and calcium carbonate filler.

Detailed Description of the Invention

The process of the present invention is useful on grades of paper that contain filler. The present invention is especially useful on grades of paper that are produced from mechanical pulps and contain calcium carbonate.

Calcium carbonate fillers that are useful in the present invention include, but are not limited to, any calcium carbonate containing mineral, for example, limestone, chalk, dolomite, and synthetically produced precipitated calcium carbonate. Other mineral fillers useful in the present invention include talcs, clays, and synthetic silicon based fillers. The filled paper is produced using standard papermaking techniques well known in the art. The filled paper may contain from about 1 percent to about 40 percent by weight filler. The preferred weight of the filler in the paper is dependent upon the particular grade of paper being produced.

Bleaching agents useful in the method of the present invention may be any type of bleaching agent. Bleaching agents especially useful in the method of the present invention are selected from the group consisting of hydrogen peroxide, sodium borohydride, and sodium hydrosulfite. The bleaching agents may be applied as an aqueous solution containing from about 0.1 percent by weight to about 50

- 5 -

percent by weight bleaching agent. Preferably, from about 0.1 percent by weight to about 5 percent by weight based on the weight of the paper is used. More preferably, the level of treating agent is from about 0.1 percent by weight to about 2 percent by weight. The bleaching agent may be applied to the paper after it is produced, such as for example, at the size press or rewinders.

10 It is believed that when paper containing calcium carbonate is bleached with hydrogen peroxide, the alkalinity of the calcium carbonate activates the hydrogen peroxide, resulting in a greater improvement in
15 brightness. What is being suggested here is a theory of why the method of the present invention allows for the bleaching of calcium carbonate containing paper. It should be accepted only as a theory and should not under
20 any conditions whatsoever be employed to limit the scope of the present invention, which is further illustrated by the Examples which follow, and more specifically defined by the Claims.

25 Examples

Example 1

Comparative Turbulent-Pulse Former (manufactured by Paper Research Materials, Inc., Camas, WA) handsheets were prepared using a pulp prepared from 100 percent deinked newsprint supplied by Garden State Paper in Garfield, New Jersey. The pulp was diluted with deionized water to a consistency of about 0.5 percent. Shear speed on the Turbulent Pulse Former was
30 1000 RPM. Retention agent (high molecular weight cationic or anionic polyacrylamide) was
35 added at about 0.05 percent. Three sets of 40-

- 6 -

pound (basis weight) handsheets were prepared containing no filler, 5.5 percent ANSILEX (calcined clay) filler, and 5.6 percent precipitated calcium carbonate filler. The

5 sheets were pressed using a nip pressure of 25 psi and dried on a rotating chrome-plated drum at a temperature of 125°C. The sheets were conditioned at 50 percent relative humidity and 23°C. for a minimum of 24 hours prior to

10 testing. The brightness of the resulting papers was tested using TAPPI test method T452-OM92. The handsheets were subjected to a bleaching treatment of either sodium borohydride or sodium hydrosulfite, in aqueous solution for 1 minute.

15 The bleached handsheets were then pressed and dried again for re-testing. The results are shown in Table 1.

- 7 -

TABLE 1

Handsheet	Bleaching Treatment		
	None	1 lb./ton NaBH_4	20 lbs./ton $\text{Na}_2\text{S}_2\text{O}_4$
N Filler (Blank)	55.0	55.3	55.3
5.5 % ANSILEX Filled (Calcined Clay)	59.1	60.1	59.8
5.6 % Precipitated Calcium Carbonate Filled	56.5	57.9	59.3

Table 1 shows improved brightness is obtained by bleaching clay or calcium carbonate containing papers.

Example 2

Comparative Turbulent-Pulse Former
handsheets were prepared from a furnish of
Miramichi Dry Groundwood pulp and deionized
5 water. The pulp was mechanically milled on a
Disintegrator for 25 minutes and then blended
for 2 minutes, after adjusting the pulp
consistency to 0.55 percent using deionized
water. Retention agent (high molecular weight
10 cationic or anionic polyacrylamide) was added at
about 0.05 percent. The sheets were filled with
either precipitated calcium carbonate or chalk
at target filler levels of 5 and 10 percent.
The handsheets were pressed, dried, and
15 conditioned as described in Example 1 prior to
testing. The sheets were then subjected to a 1
minute bleaching treatment using 2.5 ml of 0.11
percent hydrogen peroxide solution (10 lb./ton
bleach) or 2.5 ml. of 0.22 percent hydrogen
20 peroxide solution (20 lbs./ton bleach). The
sheets were then pressed, dried, and conditioned
as in Example 1 prior to re-testing. The
results are shown in Table 2.

TABLE 2

HYDROGEN PEROXIDE BLEACHING							
Sheet Type	% Filler	PH	Basis Wt. (lbs/3000 Ft ²)	Brightness No Bleach	Brightness 10 lbs/ton Bleach	Brightness 20 lbs/ton Bleach	Increase in Brightness (20 lbs/ton)
Precipitated Calcium Carbonate	10.6	9.5	41.0	54.6	56.9	57.9	+3.3
Fax Chalk	4.7	6.3	42.3	55.0	55.1	55.9	+0.9

- 10 -

Example 3

In the same manner as described in Example 2, Turbulent-Puls Former handsheets were prepared using a furnish prepared from Miramichi Dry Groundwood pulp and deionized water at a consistency of 0.55 percent. Retention agent was added at 0.05 percent. The sheets contained precipitated calcium carbonate or calcined clay or chalk or talc as fillers, at filler target levels of 5 and 10 percent. The sheets were pressed, dried, and conditioned as in Example 2 prior to testing. The sheets were then subjected to a 31 minute treatment of 2.5 ml of either 0.11 percent (10 lbs/ton bleach) or 2.5 ml of 0.165 percent (15 lbs/ton bleach) aqueous sodium hydrosulfite. The bleached sheets were then pressed, dried, and conditioned as in Example 2 prior to re-testing. The results are shown in Table 3.

TABLE 3

SODIUM HYDROSULFITE BLEACHING							
Sheet Type	% Filler	PH	Basic Wt.	Brightness No Bleach	Brightness 10 lbs/ton Bleach	Brightness 15 lbs/ton Bleach	Increase in Brightness (10 lbs/ton)
Base Stock (No filler)	0	5.4	41.0	55.0	57.7	57.2	+2.7
Precipitated Calcium Carbonate	10.0	8.8	40.8	55.1	60	60.1	+4.9
ANSILEX Calcined Clay	5.4	5.4	41.0	58.4	61.5	61.6	+3.1
Faxe Chalk	5.0	6.3	41.4	55.8	60.1	60.1	+4.3
Kanzaki Talc	4.8	5.8	41.0	55.4	58.8	58.9	+3.4

- 12 -

As can be seen in the preceding
Examples, bleaching filled paper results in
improved paper brightness. This novel method is
simple, efficient, and readily adaptable to most
5 paper producing processes.

- 13 -

C L A I M S

1. A method of improving the brightness
of filled paper comprising treating a filled
paper with an effective amount of bleaching
5 agent selected from hydrogen peroxide, sodium
borohydride and sodium hydrosulfite.
2. The method of claim 1, wherein the
paper filler is calcium carbonate and the
bleaching agent is sodium borohydride, hydrogen
10 peroxide, or sodium hydrosulfite.
3. The method of claim 1, wherein the
paper filler is selected from the group
consisting of calcium carbonate, clay, talc, and
synthetic silicon based fillers and wherein the
15 bleaching agent is sodium hydrosulfite.
4. A method of improving the brightness
of a calcium carbonate-containing paper
comprising treating the paper with an effective
amount of a bleaching agent containing hydrogen
20 peroxide.
5. An improved paper prepared according
to any one of the preceding claims.

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 D21C9/10 D21H21/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,2 510 595 (MCEWEN ET AL.) 6 June 1950 cited in the application see example 1	1,5
Y	---	3
Y	TAPPI, vol. 48, no. 2, February 1965 ATLANTA US, pages 65-72. RAPSON ET AL. 'Paper bleaching-A new process' see page 69	3
A	---	
	DE,B,12 93 019 (STIFTELSEN WALLBOARDINDUSTRIENS FORSKNINGSINSTITUT) 17 April 1969 see the whole document ---	1-3,5

	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- * 'A' document defining the general state of the art which is not considered to be of particular relevance
- * 'E' earlier document but published on or after the international filing date
- * 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * 'O' document referring to an oral disclosure, use, exhibition or other means
- * 'P' document published prior to the international filing date but later than the priority date claimed

- * 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * 'Z' document member of the same patent family

Date of the actual completion of the international search

9 April 1996

Date of mailing of the international search report

02.05.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Bernardo Noriega, F

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-2510595	06-06-50	CH-A- 265855 FR-A- 951863 GB-A- 626794	15-11-49
DE-B-1293019		GB-A- 931856 NL-A- 272946	
WO-A-9322501	11-11-93	FI-C- 90680 AU-B- 3955193 CA-A- 2134072	10-03-94 29-11-93 11-11-93

PCT/US 95/14995

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,93 22501 (KYMI PAPER MILLS LTD) 11 November 1993 see the whole document -----	1,2,4,5